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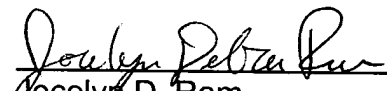
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The Examiner is invited to contact the undersigned at 202-220-4200 to discuss any matter regarding this application.

Respectfully submitted,

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PATENT ABSTRACTS OF JAPAN

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(54) HIGHLY DURABLE POLYBENZAZOLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polybenzazole composition, a fiber, and a film that have a high strength retention even after restored at a high temperature and high humidity for a long time.

SOLUTION: The highly durable polybenzazole composition, the fiber, and the film contain a basic material that dissolves in water or a hydrophilic solvent such as guanidines and triazoles.

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CLAIMS

[Claim(s)]

- [Claim 1] The high endurance polybenzazole constituent characterized by containing an alkali.
- [Claim 2] The high endurance polybenzazole constituent according to claim 1 characterized by an alkali being an organic compound.
- [Claim 3] The high endurance polybenzazole constituent according to claim 1 characterized by being the organic compound which an alkali dissolves in water or a hydrophilic solvent.
- [Claim 4] The high endurance polybenzazole constituent according to claim 1 with which an alkali is characterized by being guanidine, triazoles, quinoxaline, piperidines, aniline, pyridines, or cyanuric acid.
- [Claim 5] High endurance polybenzazole fiber characterized by consisting of a polybenzazole constituent of claim 1.
- [Claim 6] The high endurance polybenzazole film characterized by consisting of a polybenzazole constituent of claim 1.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the fiber or the film which consists of a high endurance polybenzazole constituent which makes polybenzazole come to contain the stabilizing agent which gives the preservation stability which was excellent to polybenzazole, and this polybenzazole constituent.

[0002]

[Description of the Prior Art] The fiber which consists of a polymer (it is hereafter called polybenzazole) of the poly benzooxazole (PBO), polybenzimidazole (PBI), or polybenzothiazole (PBT) as a high heatproof and high powerful fiber is known.

[0003] Usually, polybenzazole fiber is manufactured by carrying out liquid crystal spinning, using a mineral acid as a solvent. The polymer dope which came out of the spinning nozzle goes into a rinsing process, and a mineral acid is extracted in a water layer. At this rinsing process, yarn passes along the water-solution tub of inorganic base nature compounds, such as a sodium hydroxide, after being washed with water thoroughly, and the mineral acid which remains without being extracted in yarn is neutralized. Then, it is washed again. It is very important that a basic compound is given so that it may be neutralized to the interior of yarn. When the amount of grants of a rinsing condition and an inorganic base nature compound is changed by the cause to some extent, the internal environment of yarn shifts to an acidity or basicity side. When it remains in a form with a mineral acid inadequate in neutralization in yarn and is put to the bottom of an elevated temperature and high humidity for a long time, as for polybenzazole fiber, the tensile strength tends to fall.

[0004]

[Problem(s) to be Solved by the Invention] Then, even when it remains in a form with a certain reason inadequate [a mineral acid] in neutralization, polybenzazole fiber and a film with the small powerful fall by having been put to the bottom of an elevated temperature and high humidity for a long time are desired. This invention makes it a technical problem for this powerful fall to obtain small polybenzazole.

[0005]

[Means for Solving the Problem] this invention persons came to complete this invention at last, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem. That is, this invention consists of the following configuration.

1. High endurance polybenzazole constituent characterized by containing alkali.
2. High endurance polybenzazole constituent of the 1st publication of the above characterized by alkali being organic compound.
3. High endurance polybenzazole constituent of the 1st publication of the above characterized by being organic compound which alkali dissolves in water or hydrophilic solvent.
4. High endurance polybenzazole constituent of the 1st publication of the above with which alkali is characterized by being guanidine, triazoles, quinazoline, piperidines, aniline, pyridines, or cyanuric acid.
5. High endurance polybenzazole fiber characterized by consisting of polybenzazole constituent of the above 1st.
6. High endurance polybenzazole film characterized by consisting of polybenzazole constituent of the above 1st.

Hereafter, this invention is explained in full detail.

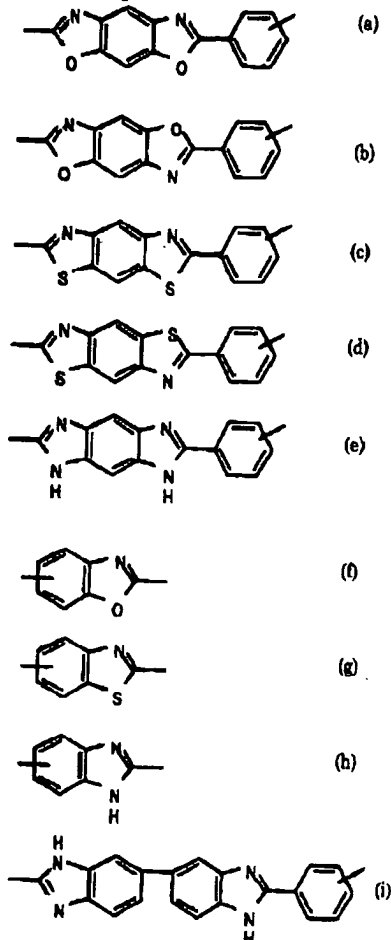
[0006] As guanidine in this invention, aminoguanidine bicarbonate, 1, 3-bis(2-benzothiazolyl) guanidine, 1,3-diphenylguanidine, 1, 3-JI (o-toluy) guanidine, 1 and 2, 3-triphenyl guanidine, etc. are raised. As triazoles, 2-(2-hydroxy-5-methylphenyl) benzotriazol, 3-amino-1,2,4-triazole, 2-[2-hydroxy-3-(3, 4, 5, 6-tetrahydro phthalimide methyl)-5-methylphenyl] benzotriazol, 2-(3, 5-G tert-butyl-2-hydroxyphenyl) benzotriazol, etc. are mentioned. As quinazoline, a piperazine etc. is raised as piperidines to which quinazoline -2, 4-dione, etc. are raised. As aniline, an aniline, an o-hydroxy aniline, o-phenoxy aniline, a p-hydroxy aniline, etc. are raised. A pyridine etc. is raised as pyridines. Or isocyanuric acid etc. is raised as cyanuric acid. There may also be concomitant use of one or two compounds or more of these basic organic compounds. An addition is 0.1% - 10% preferably 0.01% to 20% to polybenzazole. Of course, this invention technical contents are not limited to these.

[0007] The polybenzazole in this invention means the polymer more than a kind chosen from the poly benzooxazole (PBO), polybenzothiazole (PBT), or polybenzimidazole (PBI). In this invention, PBO needs to say the polymer containing the oxazole ring combined with the aromatic series radical, and the aromatic series radical does not necessarily need to be the benzene ring. Furthermore, the polymer which PBO becomes from the unit of two or more oxazole rings combined with Pori (phenylene benzoscrew oxazole) or an aromatic series radical is contained widely. The same view is applied also to PBT or PBI moreover, PBO and PBT — and — or the mixture of two or the polybenzazole polymers beyond it, such as a block of the mixture of PBI and PBO, PBT and PBI or a random copolymer, a copolymer, and block polymer are also contained. Preferably, polybenzazole is a rye OTORO pick liquid crystal polymer (liquid crystal is formed by specific concentration among a mineral acid), and its poly benzooxazole is desirable in this invention.

[0008] As a structural unit included in a PBZ polymer, it is preferably chosen from a rye OTORO pick liquid crystal polymer. A monomeric unit consists of the monomeric unit indicated by structure-expression (a) - (i).

[0009]

[Formula 1]



[0010] The solution (it is called a polymer dope) of a polybenzazole polymer can be easily prepared by carrying out the polymerization of the polymer in an acidic solvent. It is a mineral acid preferably as a solvent, for example, although there is a sulfuric acid, methanesulfonic acid, or polyphosphoric acid, it is polyphosphoric acid most preferably. The polymer concentration in a dope is 1 - 20% preferably 1 to 30%.

[0011] In this invention, a polymer or a suitable copolymer, and a suitable dope are compounded by the well-known approach. For example, it is indicated by Wolfe's and others U.S. Pat. No. 4,533,693 specification (1985, 8, 6), Sybert's and others U.S. Pat. No. 4,772,678 specification (1988, 9, 22), the U.S. Pat. No. 4,847,350 specification (1989, 7, 11) of Harris, or Gregory's and others U.S. Pat. No. 5,089,591 specification (1992, 2, 18). When it summarizes, a suitable monomer reacts in the acid solution of dehydration nature by the non-oxidizing quality, and is made to react to it by the non-oxidizing atmosphere according to gradual or raising temperature with a fixed programming rate from about 60 degrees C of bases of high-speed churning and high shear conditions to 230 degrees C.

[0012] When manufacturing fiber, a dope is extruded from a spinneret, is extended in space, and is formed in a filament. The suitable manufacturing method is indicated by the bibliography and the U.S. Pat. No. 5,034,250 specification which were described previously. The dope which came out of the spinneret goes into the space between a spinneret and a washing bus. Although this space is generally called the air gap, it is not necessary to be air. Without this space removing a solvent, it needs to be filled with the dope and the solvent which does not react, for example, air, nitrogen, an argon, helium, a carbon dioxide, etc. are mentioned.

[0013] The filament behind spinning is washed in order to avoid too much extension, and some solvents are removed. And it is washed further and is suitably washed by neutralization and the pan by inorganic base nature matter, such as a sodium hydroxide. Almost all solvents are removed even in this phase. Washing here is being compatibility to the mineral acid which is dissolving the polybenzazole polymer, contacting fiber or a filament into the liquid which does not serve as a solvent to a polybenzazole polymer, and removing an acid solvent from a dope. There is mixture of water, water, and an acid solvent as a suitable penetrant remover object. A filament is desirable and 8000 ppm or less of residual mineral-acid concentration are washed by 5000 ppm or less still more preferably. Then, as for a filament, desiccation, heat treatment, rolling up, etc. are performed if needed. Polybenzazole fiber is applicable to a rope, a cable, a fiber reinforced composite material, or incised-wound-proof garments.

[0014] When manufacturing a film, a uniaxial orientation film is made by extruding a viscous dope on a rotating drum as typically indicated by the U.S. Pat. No. 4,487,735 specification etc. This is extruded as a tube and biaxial orientation is carried out an entrainment or by pushing in on a mandrel. Subsequently, a film can be made to form by dipping underwater and making it solidify. And a solvent is removable by washing further.

[0015] It is not limited especially as the approach, i.e., a method of making polybenzazole contain said alkali, of obtaining this invention constituent, but can be made to contain in front of the polymerization phase of polybenzazole, the washing phase of a dope, and a desiccation process, or in a post-processing phase. As the approach of grant of the alkali in the polymerization phase of polybenzazole, in case a raw material is prepared, the approach of teaching an alkali to coincidence, and gradual or the approach of

adding an alkali at the time of the arbitration to which raise temperature and it is made to react with a fixed programming rate and the approach of adding an alkali at the time of polymerization reaction termination are desirable. The approach which dissolves an alkali in water or a hydrophilic organic solvent, and is immersed in a dope, a filament, or a film into this solution as the grant approach before the washing phase of the dope of polybenzazole or a desiccation process is desirable. As the approach of grant in the post-processing phase used as upright structure, an alkali is dissolved in a solvent, it is immersed, a solvent washes multifilament, a staple, a fabric, etc. behind, and the approach only except a solvent is desirable. 0.1 seconds or more, preferably, if the immersion time amount in the case of granting an alkali is 10 seconds or more, it can grant an amount enough for any number of seconds. Moreover, the simultaneous adding of two or more kinds of alkalis is also possible.

[0016] 50 degree C or more of ***** are fixed by usually drying below 300 degrees C after rinsing. The tensile strength retention after heat treatment has 80% or more to the polybenzazole molding object which has not given the alkali, and there are few bad influences to the polymer by heat treatment.

[0017] About the chemical existence condition or chemical operation of an alkali in the interior of fiber, it does not understand clearly. The moisture in an environment invades in polybenzazole fiber or a film under an elevated temperature and high humidity simply, and a remaining mineral acid dissociates with this moisture, and emits a proton. This invention is not restrained by this consideration although it is presumed that the fall on the strength is prevented by an alkali's catching this proton and maintaining the inside of a system at neutrality.

[0018] The evaluation approach is as follows. Evaluation of the reinforcement under an elevated temperature and high humidity was evaluated by measuring the retention of fiber before and after saving under an environment on the strength whenever [high-humidity/temperature] about fiber and a film. whenever [high-humidity/temperature] — the storage trial in the bottom — the Yamato science company make — Humidic Chamber 1G43M were used. Fiber or a film was twisted around the bobbin with a diameter of 5cm, it set in equipment, and continuous running was performed for 100 days under 80 degrees C and conditions of 80% of relative humidity.

[0019] Retention on the strength measured the fiber reinforcement before and behind storage according to JIS-L1013 with the tensile testing machine (the product made from A&D, form RTM 250) whenever [high-humidity/temperature], and ** (ed) and calculated the fiber value on the strength after an exposure test with the fiber value on the strength before a storage trial whenever [high-humidity/temperature]. About the film, after cutting into 8.5 micrometers in die length of 5cm, width of face of 1mm, and thickness, it asked for reinforcement similarly.

[0020]

[Example] Although an example is used for below and this invention is concretely explained to it, of course, it is also possible to add and carry out modification suitably [this invention / in the range which does not receive a limit according to the following example and may suit the main point of the account of order] from the first, and each of they is contained in the technical range of this invention. In addition, each characteristic value in an example was measured by the following approaches.

[0021] Film-like polybenzazole: It pressed after preparing the polyphosphoric acid solution (polymer dope) of polybenzazole in the condition of having inserted into the polytetrafluoroethylene sheet under 175 degrees C and 150kg/cm² conditions with the heat press machine. Then, it extended 3 times in 3 times and a longitudinal direction to the lengthwise direction at 130 degrees C, inserting a polymer dope into a polytetrafluoroethylene sheet. The dope was stripped off from the polytetrafluoroethylene sheet after cooling, and it rinsed until residual Lynn concentration was set to 5000 ppm or less.

[0022] Spinning: It carried out on conditions from which the diameter of a filament becomes 11.5 micrometers and 1.5 deniers, the spinning temperature of 150 degrees C — 160 micrometers of apertures, and a hole — it extruded during the 1st washing bath arranged so that a filament may be completed from the nozzle of a-340 number in a suitable location and it may be made multifilament. The quenching chamber was installed in the air gap between a spinning nozzle and the 1st washing bath so that a filament might be extended at more uniform temperature. Air gap length could be 30cm. The filament was spun in 60-degree C air. The take-up-machine rate was considered as a part for 200m/, and spinning draw magnification was set to 30. It rinsed until the residual phosphoric-acid concentration in polybenzazole fiber was set to 5000 ppm or less.

[0023] (Example 1) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzocresol oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 450g of aminoguanidine bicarbonates was dipped at 50 degrees C for 3 hours during the bath obtained by dissolving in water 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0024] (Example 2) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzocresol oxazoles of 27 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 3-amino-1,2,4-triazole 500g was dipped at 50 degrees C for 6 hours during the bath obtained by dissolving in water 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0025] (Example 3) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzocresol oxazoles of 29 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 1,3-diphenylguanidine 500g was dipped at 50 degrees C for 10 hours during the bath obtained by dissolving in acetone 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0026] (Example 4) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzocresol oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 1 and 3-bis (2-benzothiazolyl) guanidine 500g was dipped at 50 degrees C for 9 hours during the bath obtained by dissolving in acetone 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature /

of the obtained yarn] is shown in Table 1.

[0027] (Example 5) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 2-(2-hydroxy-5-methylphenyl) benzotriazol 500g was dipped at 50 degrees C for 5 hours during the bath obtained by dissolving in acetone 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0028] (Example 6) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. Quinazoline-2 and 4-dione 500g was dipped at 50 degrees C for 10 hours during the bath obtained by dissolving in acetone 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0029] (Example 7) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 29 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. Pyrazine 500g was dipped at 50 degrees C for 10 hours during the bath obtained by dissolving in water 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0030] (Example 8) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. 500g of isocyanuric acid was dipped at 50 degrees C for 9 hours during the bath obtained by dissolving in DMF 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0031] (Example 9) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 14 % of the weight of poly para-phenylene benzoscrew oxazoles of 30 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. Aniline 500g was dipped at 50 degrees C for 20 hours during the bath obtained by dissolving in water 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0032] (Example 10) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 13 % of the weight of poly para-phenylene benzoscrew oxazoles of 28 dL/g by the above-mentioned approach, and rolled round 1500m to the yarn tube. Pyridine 300g was dipped at 50 degrees C for 10 hours during the bath obtained by dissolving in water 10L, and it dried at 80 degrees C for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0033] (Example 1 of a comparison) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution carried out spinning of the spinning dope which consists of polyphosphoric acid of 88% of phosphorus-pentaoxide content to 14 % of the weight of poly para-phenylene benzoscrew oxazoles of 28 dL/g by the above-mentioned approach. This yarn was dipped for 1 minute after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained yarn] is shown in Table 1.

[0034]

[Table 1]

引っぱり強度保持率	
	%
実施例 1	85
実施例 2	84
実施例 3	82
実施例 4	80
実施例 5	84
実施例 6	85
実施例 7	85
実施例 8	84
実施例 9	82
実施例 10	80
比較例 1	45

[0035] (Example 11) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 25 dL/g, and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving 100g of aminoguanidine bicarbonates into water 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0036] (Example 12) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 24 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving 3-amino-1,2,4-triazole 100g into water 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0037] (Example 13) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 25 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving 100g of isocyanuric acid into DMF10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0038] (Example 14) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 14 % of the weight of poly para-phenylene benzoscrew oxazoles of 25 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving pyrazine 100g into water 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0039] (Example 15) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 25 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving quinazoline -2 and 4-dione 100g into acetone 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0040] (Example 16) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 23 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving aniline 100g into water 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0041] (Example 17) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 14 % of the weight of poly para-phenylene benzoscrew oxazoles of 26 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. This film-like matter was dipped for 1 minute during the bath obtained by dissolving pyridine 100g into water 10L, and it dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0042] (Example 2 of a comparison) The intrinsic viscosity measured with the 30-degree C methansulfonic acid solution made the dope which consists of polyphosphoric acid of 12 % of the weight of poly para-phenylene benzoscrew oxazoles of 25 dL/g. and 88% of phosphorus-pentaoxide content the shape of a film by the above-mentioned approach. It dried at 80 degrees C after washing with water for 4 hours. Thus, the result of having performed the storage trial whenever [high-humidity/temperature / of the obtained film] is shown in Table 2.

[0043]

[Table 2]

	強度保持率
	%
実施例 1 1	63
実施例 1 2	70
実施例 1 3	68
実施例 1 4	66
実施例 1 5	73
実施例 1 6	64
実施例 1 7	67
実施例 1 8	68
実施例 1 9	60
実施例 2 0	65
比較例 2	42

[0044] The polybenzazole fiber and the film with which the basic organic compound was given are understood that the retention on the strength in the bottom is [whenever / high-humidity/temperature] high so that more clearly than Tables 1 and 2.

[0045] [Effect of the Invention] Since its retention on the strength is high even after the constituent, the fiber, and the film concerning this invention are kept downward whenever [high-humidity/temperature] for a long time, they are contributing [can expand the field of the invention by leaps and bounds, and] to the industrial world size.

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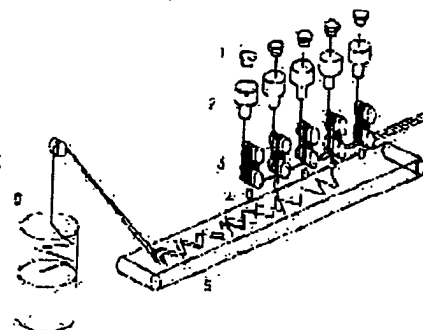
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(54) PRODUCTION OF POLYBENZAZOLE FIBER AND PRODUCTION DEVICE THEREFOR

(57)Abstract

PROBLEM TO BE SOLVED: To efficiently reduce a basic unit and to obtain a polybenzazole fiber excellent in productivity by using a polybenzazole prepared by solution polymerization in an acid solvent, extruding a dope filament from a spinneret and continuously supplying the dope filament to a spinning process for staple when an end breakage occurs.

SOLUTION: A polybenzazole polymer is obtained by solution polymerization in an acid solvent, a polymerization solution is directly extruded as spinning dope from a spinneret 1. A spinning position having caused an end breakage is continuously supplied to a spinning process for staple. A prepared dope filament is coagulated/washed/dried to give a polybenzazole fiber. The fiber is obtained by using a production apparatus equipped with a conveyor 5 transporting a fiber having passed a coagulating bath 2 to a staple can 6, below take-off rollers 3 arranged at an outlet of the coagulating bath 2 of each spinning position. A suction device 4 for fiber is preferably installed between the take-off rolls 3 and the conveyor 5.



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[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the polybenzazole fiber which carries out the solution polymerization of the polybenzazole polymer in an acid solvent, and is characterized by to present the production process for staples with a dope filament continuously, without stopping supply of a spinning dope in the approach of solidifying, washing and drying the dope filament which extruded and was obtained from the spinneret, and manufacturing a polybenzazole filament when the thread breakage occurs by considering a polymerization solution as a direct spinning dope.

[Claim 2] The manufacture approach of the polybenzazole fiber according to claim 1 characterized by presenting the silk manufacture process for staples only with the spindle which extruded the dope filament from two or more spinnerets, and the thread breakage generated continuously.

[Claim 3] The manufacturing installation of the polybenzazole fiber characterized by forming the conveyor for conveying the line of thread which passed the coagulation bath in the lower part of the dealings roll arranged at the outlet of the coagulation bath of each spindle to staple KENSU in the manufacturing installation of the polybenzazole filament which consisted of two or more spinning spindles.

[Claim 4] The manufacturing installation of the polybenzazole fiber according to claim 3 characterized by forming the aspirator of the line of thread which passed the coagulation bath between a taking over roll and a conveyor.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the fiber of high intensity and the rate poly benzoxazole of high elasticity. It is related with the approach and equipment which manufacture the fiber of high intensity and the rate poly benzoxazole of high elasticity by the low material unit in more detail.

[0002]

[Description of the Prior Art] Polybenzazole fiber has fiber twice [more than] the elastic modulus [the reinforcement and the elastic modulus] of poly para-phenylene terephthalamide which are the representation of super fibers by which current marketing is carried out. Therefore, it is expected as next-generation super fibers. It is well-known to manufacture fiber from the polyphosphoric acid solution of polybenzazole polymer. For example, about the spinning approach, there are a U.S. Pat. No. 5296185 number and a U.S. Pat. No. 5294390 number, about the heat treatment approach, a U.S. Pat. No. 5288445 number is made about the desiccation approach, and the proposal is made for JP, 7-197307, A. Moreover, the United States patent application 008/No. 425493 is proposed also about the process of a staple. Although polybenzazole fiber can be fundamentally produced by these production technologies, it is necessary to actually solve many problems which **** by the thread breakage generates a spindle when operating a **** production line, and lower a material unit.

[0003]

[Problem(s) to be Solved by the Invention] it faces manufacturing the spinning dope which consists of polybenzazole and polyphosphoric acid using many spinning spindles by the so-called polymerization direct spinning method, and polymer supply of the spindle which the thread breakage generated so that it might be carried out by the usual wet spinning is stopped — it is — it is — it is very difficult to store as a dope for spinning separately. If polymer supply is suspended to this spindle, in order to cause fluctuation of the polymer quality in a polymerization process and to avoid this, when the polymer for this spindle is stored, on a scale with industrial using the spinning dope which stored separately the spinning dope which consists of polybenzazole and polyphosphoric acid since viscosity exceeded 100,000poise also at spinning temperature easily highly extremely unlike the dope for the usual wet spinning, it is because it is difficult. In this invention, such technical difficulty is conquered and the high-speed silk manufacture technique for making the fall of the material unit accompanying thread-breakage **** for polybenzazole fiber into min and a facility are offered.

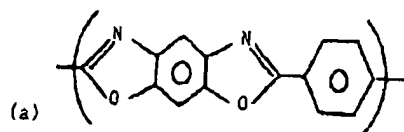
[0004]

[Means for Solving the Problem] this invention persons are high speeds, and studied production of polybenzazole fiber wholeheartedly for the purpose of manufacturing cheaply, and found out the solution means. Namely, the manufacture approach of the polybenzazole fiber which carries out the solution polymerization of the polybenzazole polymer in an acid solvent, and is characterized by to present the production process for staples with a dope filament continuously, without stopping supply of a spinning dope in the approach of solidifying, washing and drying the dope filament which extruded and was obtained from the spinneret, and manufacturing a polybenzazole filament when the thread breakage occurs by considering a polymerization solution as a direct spinning dope. The manufacturing installation of the polybenzazole fiber characterized by forming the conveyor for conveying the line of thread which passed the coagulation bath in the lower part of the dealings roll arranged at the outlet of the coagulation bath of each spindle to staple KENSU in the manufacturing installation of the polybenzazole filament which consisted of two or more spinning spindles.

[0005] This invention is explained to a detail below. the fiber which turns into polybenzazole fiber in this invention from a polybenzazole polymer — saying — polybenzazole (PBZ) — the poly benzoxazole (PBO) homopolymer, a polybenzothiazole (PBT) homopolymer, and the random of them PBO and PBT — sequential or a block copolymerization polymer is said. here — the poly benzoxazole, polybenzothiazoles, and those random — sequential or a block copolymerization polymer For example "Liquid Crystalline Polymer Compositions and Process and Products" U.S. Pat. No. 4703103, such as Wolfe (October 27, 1987), A "Liquid Crystalline Polymer Compositions and Process and Products" U.S. Pat. No. 4533692 number (August 6, 1985), "Liquid Crystalline Poly (2, 6-Benzothiazole) Composition and Process and Products" U.S. Pat. No. 4533724 (August 6, 1985), "Liquid Crystalline Polymer Compositions and Process and Products" U.S. Pat. No. 4533693 (August 6, 1985), Evers Thermooxidative-ly ~ Stable Articulated p-Benzobisoxazole and p-Benzobisthiazole Polymers" U.S. Pat. No. 4539567 (November 16, 1982). It is indicated by "Method for making Heterocyclic Block Copolymer" U.S. Pat. No. 4578432 (March 25, 1986), such as Tasi, etc. As a structural unit included in a PBZ polymer, it is preferably chosen from a rye OTORO pick liquid crystal polymer. A monomeric unit consists of a monomeric unit indicated by structure-expression (a) - (h), and consists of a monomeric unit essentially chosen from structure-expression (a) - (c) still more preferably.

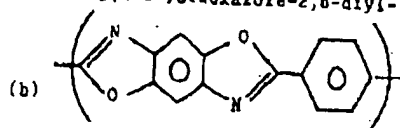
[0006]

[Formula 1]



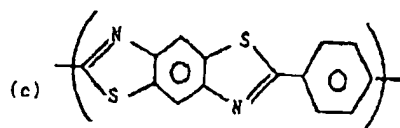
cis-polybenzoxazole

Poly[benzo(1,2-d:5,4-d')bisoxazole-2,6-diyl-1,4-phenylene]

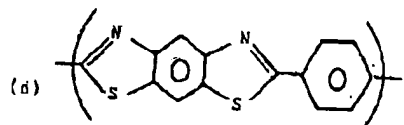


trans-polybenzoxazole

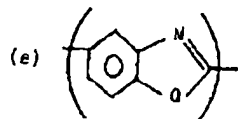
Poly[benzo(1,2-d:4,5-d')bisoxazole-2,6-diyl-1,4-phenylene]



trans-polybenzothiazole

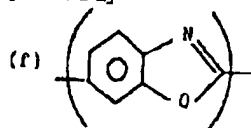


cis-polybenzothiazole

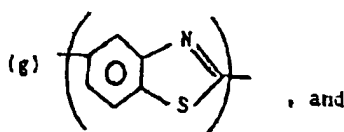


AB-PBD
Poly(2,5-benzoxazole)

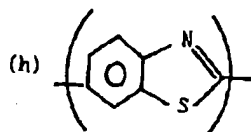
[0007]
[Formula 2]



AB-PBD
Poly(2,6-benzoxazole)



Poly(2,5-benzothiazole)



Poly(2,6-benzothiazole)

[0008] As a suitable solvent for forming the dope of a PBZ polymer, the acid of a non-oxidizing quality which may dissolve cresol and its polymer is contained. As an example of a suitable acid solvent, polyphosphoric acid, methansulfonic acid and high-concentration sulfuric acids, or those mixture are mentioned. Solvents suitable furthermore are polyphosphoric acid and methansulfonic acid. Moreover, a most suitable solvent is polyphosphoric acid.

[0009] The polymer concentration in a solvent is about 7 % of the weight at least preferably, and is at least 14 % of the weight most preferably at least 10% of the weight still more preferably. The maximum concentration is limited by the handling nature after [actual] calling it the solubility of a polymer, and dope viscosity. For those marginal factors, polymer concentration does not exceed 20 % of the weight by usual.

[0010] A suitable polymer, a copolymer, or a dope is compounded by well-known technique. For example It is compounded by the approach indicated by U.S. Pat. No. 4772678 numbers (September 20, 1988), such as U.S. Pat. No. 4533693 (August 6, 1985), such

as Wolfe, and Sybert, and U.S. Pat. No. 4847350 (July 11, 1989) of Harris. a PBZ polymer — Gregory etc. — according to U.S. Pat. No. 5089591 (February 18, 1992) — the inside of the acid solvent of dehydration nature — the macromolecule quantification with a high reaction rate is comparatively possible under an elevated temperature and a high shear condition.

[0011] Thus, the dope by which a polymerization is carried out is supplied to the spinning section, and is usually breathed out at the temperature of 100 degrees C or more from a spinneret, a mouthpiece — you may be other arrays although two or more arrays of pore are usually arranged the shape of a periphery, and in the shape of a grid, a mouthpiece — although especially the number of pores is not limited, the array of the spinning pore in a spinneret side needs to maintain hole density which the welding between regurgitation lines of thread etc. does not generate.

[0012] The dope of the shape of a filament breathed out in the gas of non-freezing characteristic (the so-called air gap) from this spinneret can give a draft in an air gap. It is effective to prepare the so-called quench chamber which uses a cooling wind and cools a line of thread into an air gap, in order to raise the cooling effectiveness of this line of thread, in order to obtain an early spinning rate especially.

[0013] Subsequently, this line of thread is led to coagulation liquid, and coagulation and/or extract washing are carried out. Coagulation liquid has a desirable phosphate water solution, a phosphate water solution is 50% of 10% or more phosphoric-acid concentration, and it is still more desirable that temperature is 30 degrees C or more 80 degrees C or less.

[0014] The ** Lynn concentration of the line of thread after coagulation / washing has preferably desirable 5000 ppm or less 10000 ppm or less. Moreover, especially the thing that the atomic ratio of alkali metal to Lynn which a neutralization process is included in a washing process, and the base of alkali metal is used as neutralization drugs, and remains in fiber does to 1.5 or less [0.5 or more] is not indispensable although it is desirable because of the physical-properties maintenance under post processing of fiber.

[0015] The line of thread which passed through coagulation / washing process is dried within a dryer. Spinning and coagulation, and the washed spinning yarn can be dried on said suitable conditions, without generating a void in which the fall of fiber physical properties is caused at high temperature 200 degrees C or more. It is also possible to raise temperature to step WAIZU and to dry to it, of course. As a drier, the drier of a hot calender roll, oven, and others can use.

[0016] When using the manufacture approach of this polybenzazole filament for production on a scale of being industrial, as shown in drawing 1, it produces using many spinnerets. Thus, since the thread guard of many lines of thread is carried out to the same production line at coincidence, when the thread breakage generally arises, in order not to reduce a material unit, it **** by halt of a spinning pump etc. As for the spinning of polybenzazole, it is desirable to adopt a polymerization direct spinning method by hyperviscosity. In this case, it is not desirable on the stability of a polymer to fluctuate the polymerization amount of supply corresponding to reduction of the initial complement of the spinning dope which spinning takes. Moreover, as an approach of solving the problem, it becomes a waste of a raw material to keep a thread-breakage spindle discharged, and a material unit goes up.

[0017] In order that this invention may reconcile adequate supply and productivity of a polymer, the line of thread of the spindle which took over, and installed the conveyor (5) in the lower part of a roll (3), and the thread breakage generated at the time of manufacture of a polybenzazole filament prepared in the coagulation bath (2) outlet is continuously shaken off on a conveyor with the aspirator (4) of the conveyor upper part. A network conveyor is suitable for this conveyor in order to separate a coagulation bath and a line of thread. Staple KENSU (6) is prepared in this conveyor outlet, and the line of thread of a thread-breakage spindle is taken over by KENSU. The re-thread guard of all the Rhine lines of thread is performed in the place where the thread-breakage number reached the set point in the reason that the thread-breakage number which results in the thread guard of all production-line lines of thread, of course is determined in consideration of productivity.

[0018] Thus, the line of thread of the thread-breakage spindle taken over by fixed period staple KENSU collects KENSU, and is separately washed [as well as manufacture of an above-mentioned filament] and dried by the off-line processor as two or more lines of thread. Suitably, an off-line-processing machine is the manufacturing installation of a staple, it gives crimp after desiccation to a line of thread, is cut by the rotary cutter, and produces a staple. It is also possible to process washing, desiccation, etc. on a conveyor, without changing the sequence of processing, of course and using staple KENSU. As an indispensable technique of this invention, down stream processing different from a filament production line is installed, and it is in reducing a polymer material unit.

[Example] Although an example is shown below, this invention is not limited to these examples.

The spinning dope which was obtained by the approach shown (example) United States patent No. 4533693 and which the intrinsic viscosity measured with the 30-degree C methansulfonic acid solution becomes from polyphosphoric acid of polybenzazole 14.0 (weight) % of 24.4 dL/g and 83.17% of phosphorus-pentoxide content was used for spinning, a dope — a metal — a reticulated filtering medium is passed, and a pressure up is carried out after the kneading equipment which subsequently consists of biaxial performs kneading and degassing — making — polymer solution temperature — 170 degrees C — maintaining — a hole — after spinning at 170 degrees C from spinneret 4 spindle which has a-334 number and cooling a regurgitation line of thread using a cooling wind with a temperature of 60 degrees C, it introduced into the coagulation bath. It was a part for 600m/, the spinning rate was made to solidify with 50 degrees C and 20% phosphate water solution, after it gave the spinning rate with a taking over roll and it washed the line of thread in the 2nd and 3rd extract bath, was immersed in the sodium-hydroxide solution of a decinormal, and carried out neutralization processing. Immediately after washing by the wash bath furthermore, it dried using the dryer. Similarly desiccation conditions and the acquired physical properties of fiber are shown in Table 1. After carrying out the thread breakage of the one spindle artificially among the lines of thread of these four spindles, the suction machine was used and shaken off on the network conveyor formed in the roll lower part. The line of thread dropped on KENSU from the edge of network KOMBEANO was rinsed and dried separately. The physical properties of fiber were what is not so good in the physical properties of a filament, as shown in Table 1.

[0019] After rinsing the fiber separately brought together in KENSU and giving crimp by the crimper, it cut and dried to 44mm and the staple was created. The yarn physical properties which were excellent as the spun yarn which could process it satisfactory at all in the production process, and was obtained again was shown in Table 1, when this staple was used as spun yarn through a spinning process are held, the spun yarn obtained by the approach of this invention is completely equal as a product, and it turns out that it is enough as a production system. Therefore, even if it is in a mass-production-method facility many spindles exist in one line by the approach of this invention, polybenzazole fiber can manufacture cheaply with the value near a theoretical material unit.

[0020]

[Table 1]

		正常値	糸切れ値	紡績糸
単糸特性				
単糸デニール		1.5	1.5	
強度	g/d	45	42	
弾性率	g/d	1361	1248	
伸度	%	3.6	3.6	
ステーブル特性				
クリンプ数	#/inch			4.5
クリンプ指数	%			3.2
紡績糸特性				
綿番手				20
強力	g			4238
弾性率	g/d			431
伸度	%			3.9

[0021]

[Effect of the Invention] By this invention, manufacture of polybenzazole fiber is cheaply attained on a scale of industrial.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram of the manufacturing installation of this invention.

[Description of Notations]

1. Spinneret, 2. Coagulation Bath, 3. Taking over Roll, 4. Aspirator, 5. Conveyor
6. Staple KENSU

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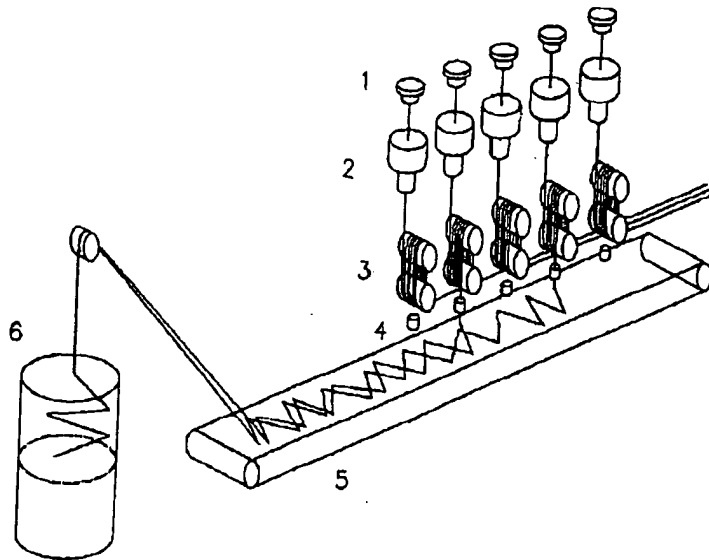
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DRAWINGS

[Drawing 1]



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